Bench-scale Fabrication of Thick Electrodes as It Relates to Performance and Industry Practices

Vince Battaglia

LBNL

June 19, 2018

Project ID #
ES232

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/31/2018
- Percent complete: 90%

Barriers

- Barriers addressed (EV)
  - A. *Cost* - $75/kWh
  - C. *Performance* - 2/1 P/E for 30 seconds at 80% DOD
  - E. *Life* - 10 years

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding for FY 2018:
  - $1 M (2.5 FTEs)

Partners

- Interactions / collaborations
  - Arkema
  - Umicore
  - Daikin America
  - BMR Program and LBNL
    - G. Liu (LBNL)
    - D. Parkinsen (LBNL)
    - D. Wheeler (BYU)
    - K. Zaghib (HQ)

Relevance: Objectives and Impact

LBNL

- Project Objective:

Establish fundamental practices in the fabrication of electrode laminates based on material and rheological properties.

  - Work this year (from Apr. ’17 to Apr. ’18):
    - Investigated the effect of drying temperature
      - On electrode morphology
      - On electrode mechanical properties
      - On electrode resistance
      - On electrode cycleability

- Relevance to VT Office:

The fabrication of thick electrodes addresses two main barriers for EV adoption *cost per kWh* and *energy density*.

Every research group fabricating cells for Battery 500 or Extreme Fast Charging or industry should be aware of the effects of drying time and temperature on the performance of thick electrodes.

- Impact:

Optimized fabrication of electrodes at the bench-top scale but at manufacturing speeds should accelerate the introduction of new technologies into cells and the rate at which advanced batteries meet accepted performance targets.

Issues of Thick Electrodes

LBNL

General Question

- Are today's batteries limited in thickness (50 to 70 μm) as a result of cell performance or manufacturing capability?
  - If one is using the standard electrode formulation and is not concerned with fast charging, today's batteries are limited by manufacturing issues

    Electrodes of 6 mAh/cm^2 are capable of C/3 discharge

    However, these electrodes demonstrate:
    - Mud-cracking when dried too fast
    - Segregation of carbon / binder and active material when dried too slow
    - A mismatch between electrode performance and mechanical performance
    - Delamination at all conditions
  - Our mission is to explore the physics that will lead to optimized mechanical and electrochemical properties of high loading electrodes (> 5 mAh/cm^2).

Fundamentally, we want to understand the relationship of the physical and chemical forces that lead to the final position of materials and potential modifications of materials and process conditions to optimize electrode capability and performance.

Technical Approach/Strategy

LBNL

To investigate modifications to materials and process conditions toward the fabrication of ultra-high loading electrodes, utilizing a suite of diagnostic tools including the ALS to determine the sources of variability of electrode performance.

Materials *Process Conditions* *Diagnostics* *Engineering Principles*

2015 → **2016** → **2017** → **2018**

Effect of material properties and processing conditions on electrode uniformity

Combinations of materials and processes that provide engineering principles to electrode manufacturing.

Combination of materials and processes that can be performed today

Over the past three years we've been able to scope out the first two topics by conventional means (lab scale battery fabrication, viscometry, bend tests, adhesion tests). We have learned that: 1) suppliers matter (impurities), 2) mixing matters (order of mixing and type), 3) molecular weight matters (viscosity, adhesion, cohesion), 5) drying temperature matters (cracking, settling), 6) calendering does not matter (although warmer temperatures allow for one pass through), Additional resources are needed to understand the physical phenomena and translate that to engineering principles.

Technical Approach/Strategy

LBNL

In the third year of this project we now turn to investigate the effect of drying temperature on electrode fabrication and performance.

- ✓ Unlike a production line where slurries are cast onto a metal foil and then pulled through a drying oven of multiple stages, we had to develop a methodology for drying electrodes formed on a drawdown coater that allowed the electrodes to dry in the same amount of time.
  - ✓ Electrodes are cast onto thin aluminum foil that is resting upon a thin aluminum plate with multiple holes drilled into it (this reduces the thermal mass of the plate allowing for faster heat up.)
  - ✓ The temperature of the oven is set at a particular temperature and a thermocouple is placed between the aluminum plate and the aluminum foil.
  - ✓ The foil is monitored for drying and the time recorded.
- ✓ Dried electrodes are then subject to testing
  - ✓ Visual inspection for mud cracking
  - ✓ Mechanical performance (adhesion and cohesion)
  - ✓ Electrochemical performance
- ✓ PVdF binders of different molecular weights are used in the investigation.

The experiments are designed to assess the effects of drying rate, temperature, gravity, surface tension, and viscosity on the final morphology and performance of high-loading cathodes.

Milestones

LBNL

Date	Milestones and Go/No-go Decisions	Status
December 2017	Develop a methodology for fabricating “thick” cathodes of NCM and establish the effect of drying temperature on electrode morphology.	Met
March 2018	Measure the mechanical and electrochemical properties of electrodes dried at different temperatures.	Met
June 2018	Measure the surface tension and the viscosity of the slurry as a function of temperature and NMP content. Determine the source of impedance of electrodes dried at different temperatures.	On schedule
September 2018	Implement advanced diagnostic techniques to identify differences in component configuration and correlate with performance.	On schedule

Technical Accomplishments

LBNL

Previous Years

1. Mixing methodology, order of components, and time strongly impact the distribution of the components

2. Assessed binders from two vendors on
   1. Solubility in NMP (some vendors have dirty solutions with poor solubility)
   2. Ability to make comparable electrodes.
   3. Electrode uniformity.

3. Slurry viscosity greatly influences the final configuration of the components

4. Assessed electrode processing conditions
   1. Casting speed
   2. Height of doctor blade

5. Assessed electrode performance (power and energy)
   - Electrode thickness
   - Electrode porosity (must keep above 35%)
     - For Li-ion, there is an optimum in power and energy with regard to thickness an porosity

6. Assessed effects of calendering at temperature
   1. Calendering at higher temperatures reduces the electrode bounce back but has little effect on the ability to compress to lower porosity. Calendering to below 40% porosity weakens, flattens, and fractures the secondary particles of NCM used for these tests.

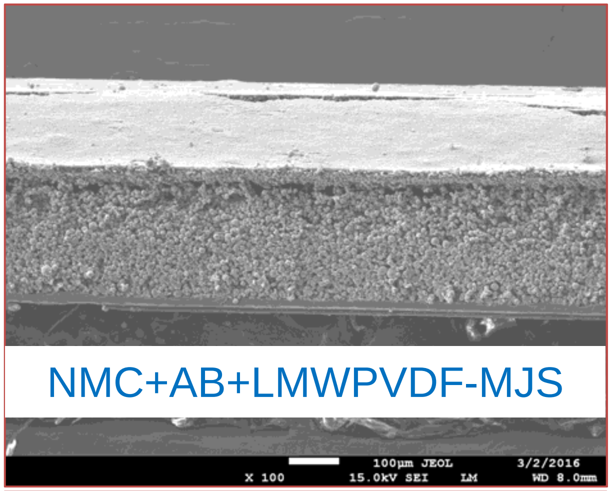
7. Assessed binder fraction
   1. The amount of polymer binder (*ca*. 3 to 4 % for electrodes at 250 μm). Too much, and the electrode is too stiff and breaks under the strain of bending; too little and the electrode has little adhesive or cohesive strength.

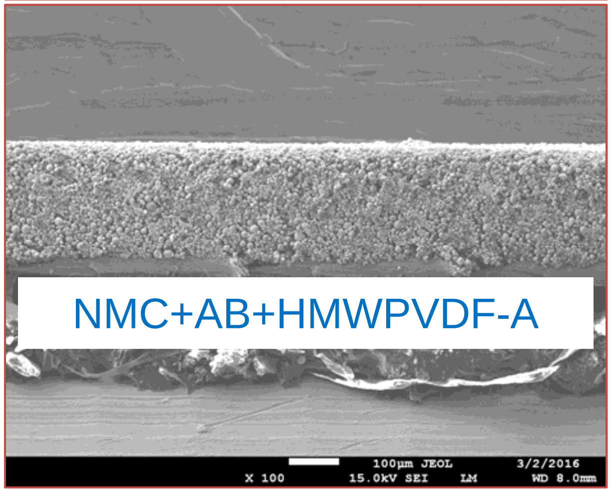
Technical Accomplishments

LBNL

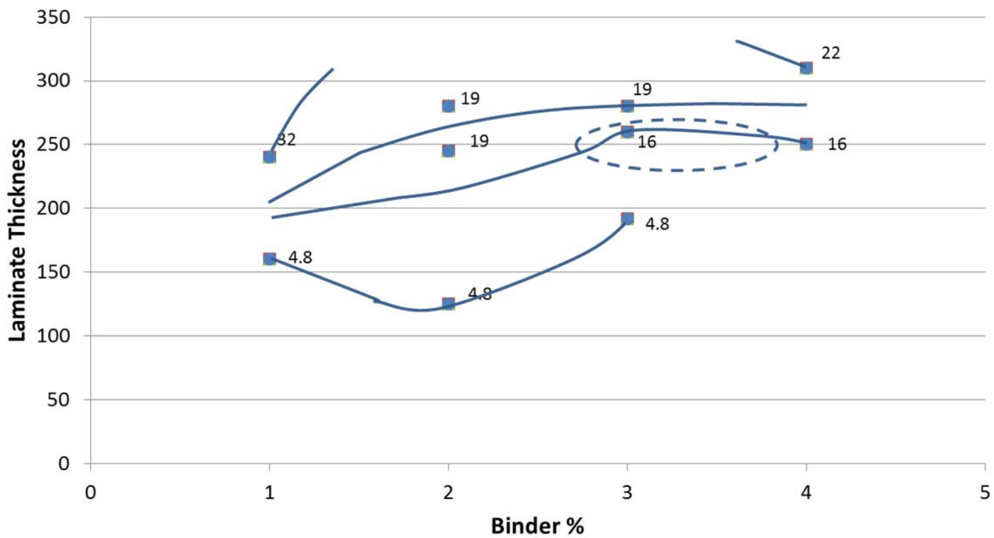
Previous Years

Drying time matters
Viscosity Matters





Quantity of inactive components matters



numbers indicate diameter of roller

- For slow drying times (overnight) need higher viscosity to prevent segregation of materials (either less NMP or higher MW binder).
- Very thick electrodes require *ca.* 3% binder.

Technical Accomplishments

LBNL

This Year

The focus of the work this year was binders of ***different molecular weights*** and the ***drying*** of thick laminates at rates approaching industry (< 10 min)

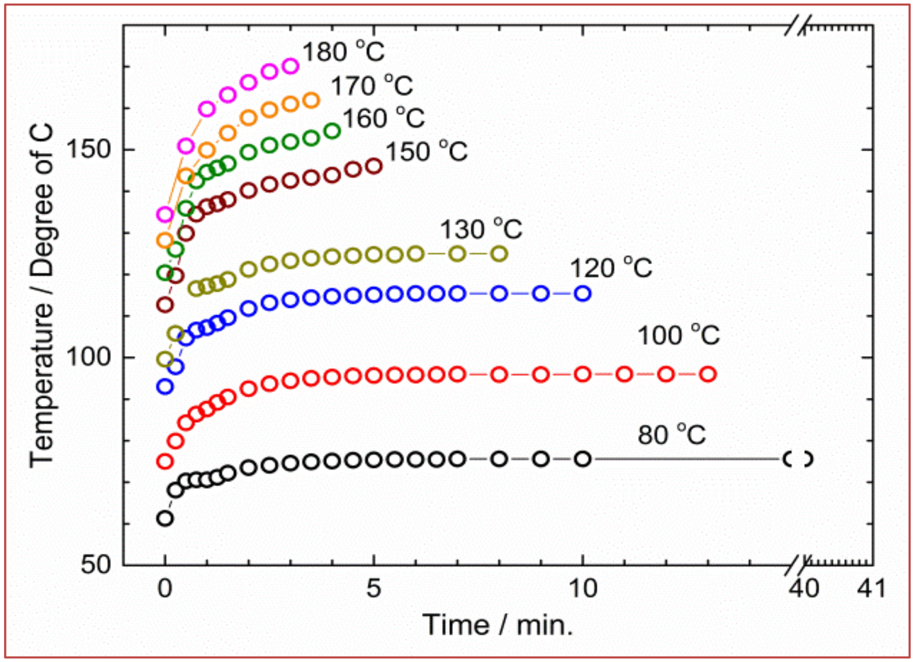
1. Developed a methodology such that the temperature of the laminates reached the temperature of the drying oven within a minute
2. Drying too fast (@ temperatures $\geq$ 145 ^{o}C) results in mud cracking and reduced mechanical strength
    - This may be related to the melt transition of the PVdF
3. Electrochemical rate performance decreases with increase in drying temperature (from 80 to 180 ^{o}C.)
    - Measured the 30 sec power pulse capability of a number of dried laminates assembled into half cells.
    - Investigated a host of binders and combinations of binders
4. Initiated an investigation of combinations of binders of different molecular weight

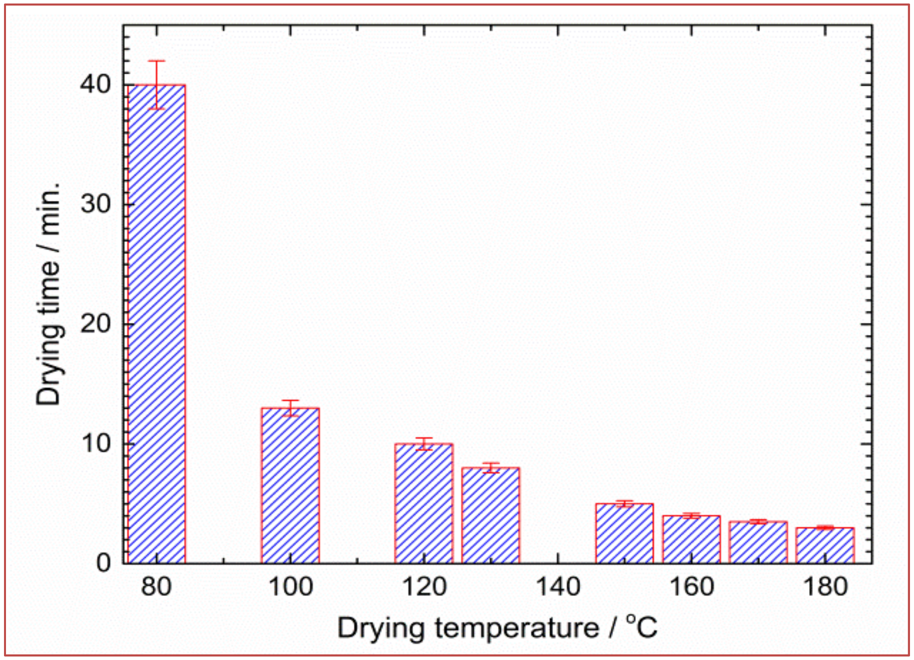
Technical Accomplishments

LBNL

<u>This Year</u>

- ✓ Process developed for casting and drying electrodes produced on a drawdown coater.
  - ✓ Advantages: can take as much time as required
  - ✓ Disadvantages: there is more thermal mass to contend with which lengthens the time to temperature.





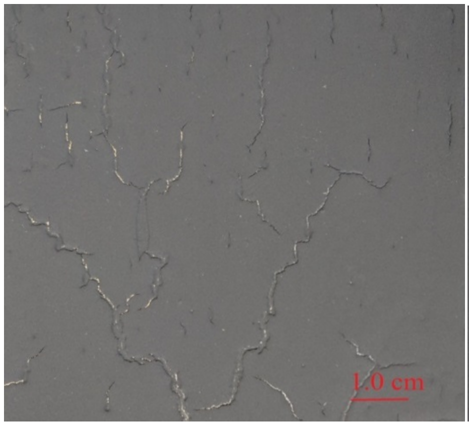
Temperatures greater than 100 ^{o}C are required to dry an electrode in less than 10 minutes.

Technical Accomplishments

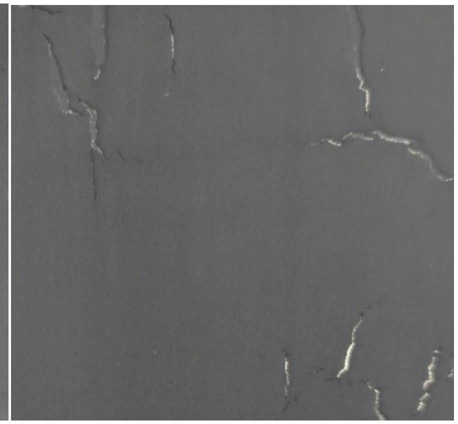
LBNL

Electrodes dried at elevated temperatures

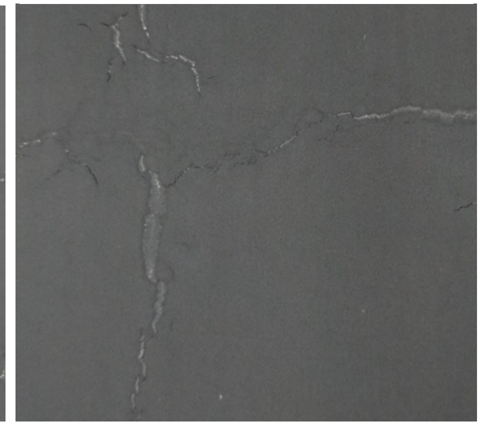
Drying t: < 3min.
Oven T: ~190 ℃



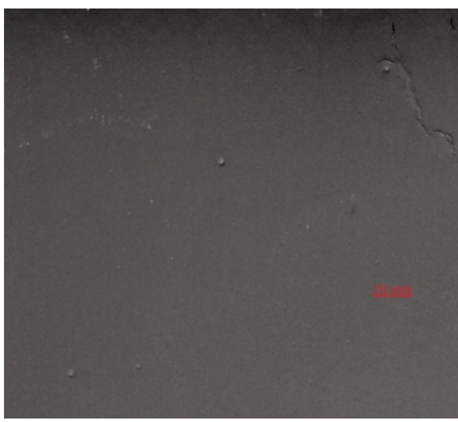
Drying t: < 4 min.
Oven T: ~170℃



Drying t: > 4min.
Oven T: ~160℃



Drying t: ~ 4 min.
Oven T: ~150 ℃



Drying t: ~ 4.5 min.
Oven T: ~145 ℃

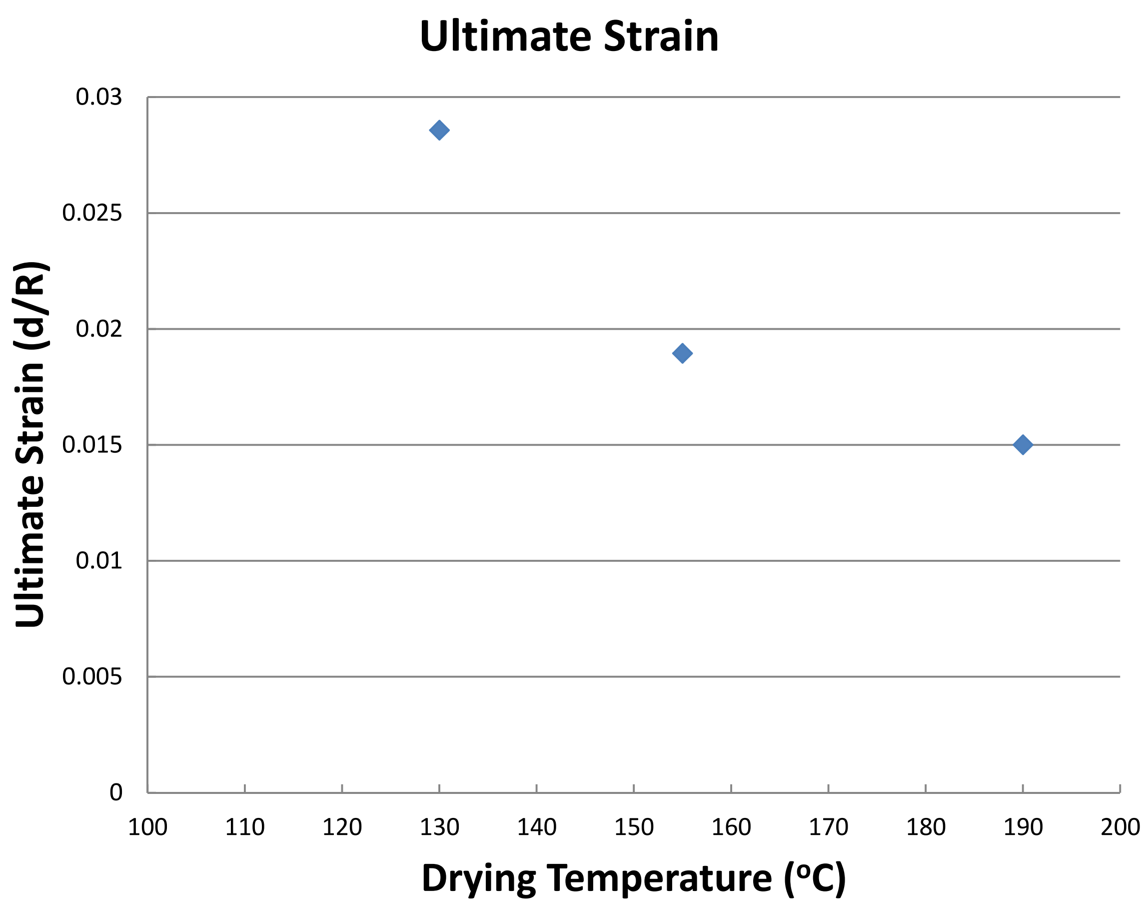
Drying t: ~ 7 min.
Oven T: ~130 ℃

Electrodes dried above 145 ℃ displayed blistering or cracking.

Technical Accomplishments

LBNL

Mechanical Performance



Electrodes dried at lower temperatures withstood higher strains on the bend test.

Technical Accomplishments

LBNL

Developed a methodology for measuring adhesion and cohesion

Adhesion measurement

Electrode face taped to block, tape applied to current collector and pulled off at 180º.

Cohesion measurement

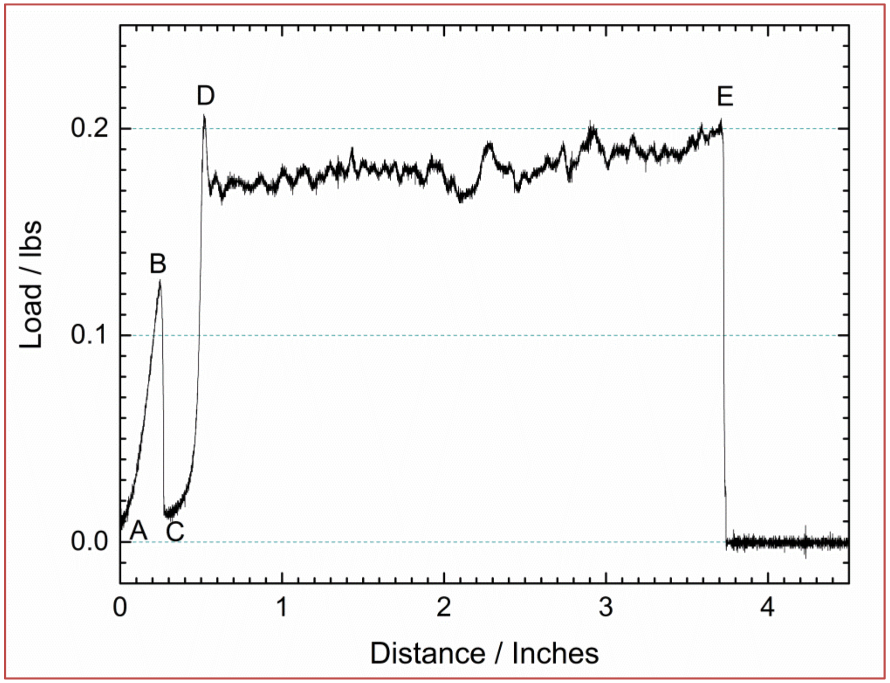
Current collector gently removed from electrode, bottom half taped to block and upper half taped to gage.

Technique successful because cohesion strength greater than adhesion.

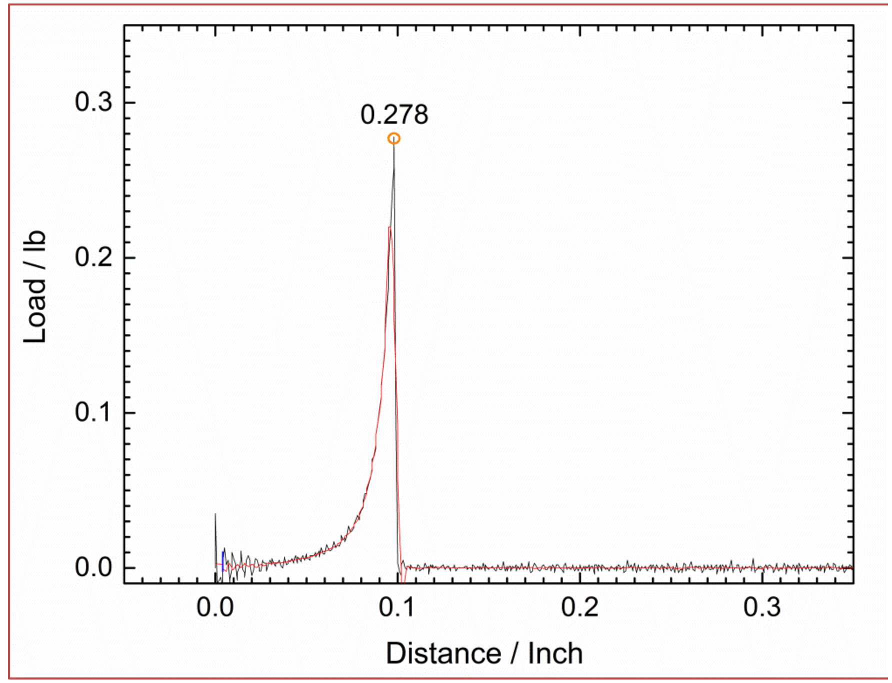
Technical Accomplishments

LBNL

Adhesion and Cohesion Sample Data



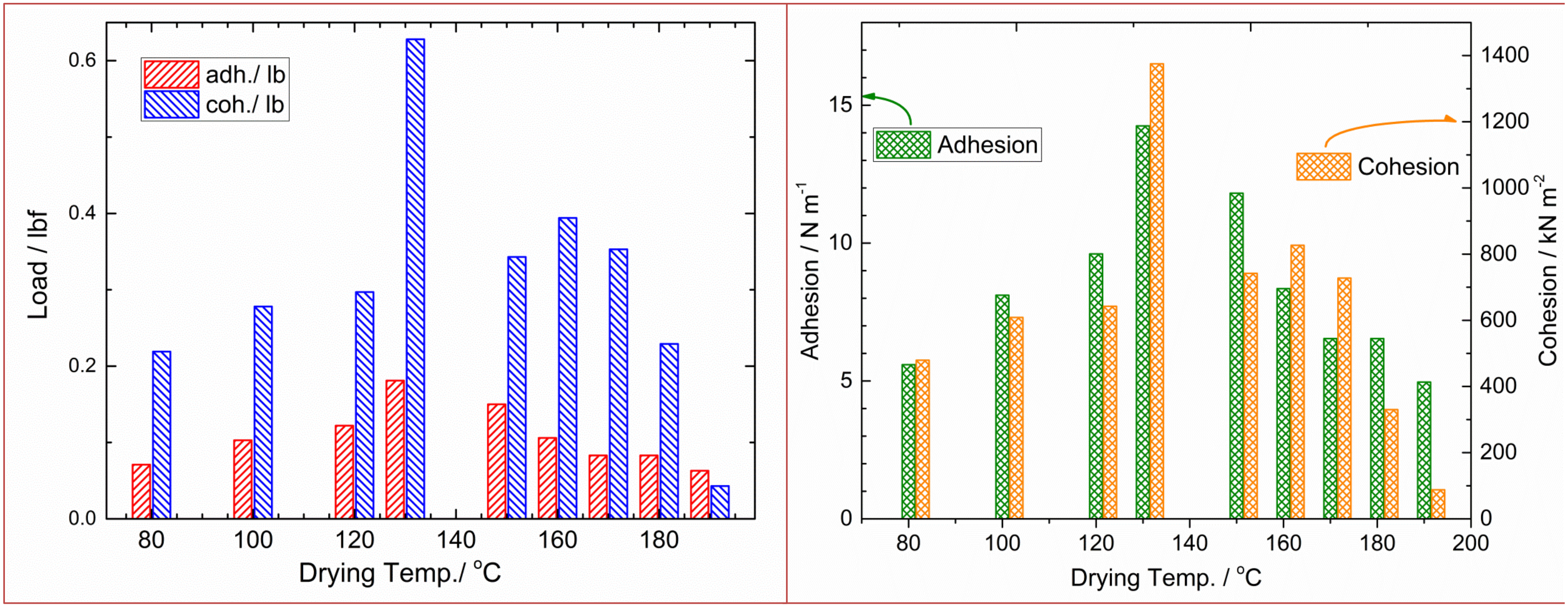
Adhesion Test Data



Cohesion Test Data

Technical Accomplishment

Cohesion and Adhesion Results
(plotted two ways)

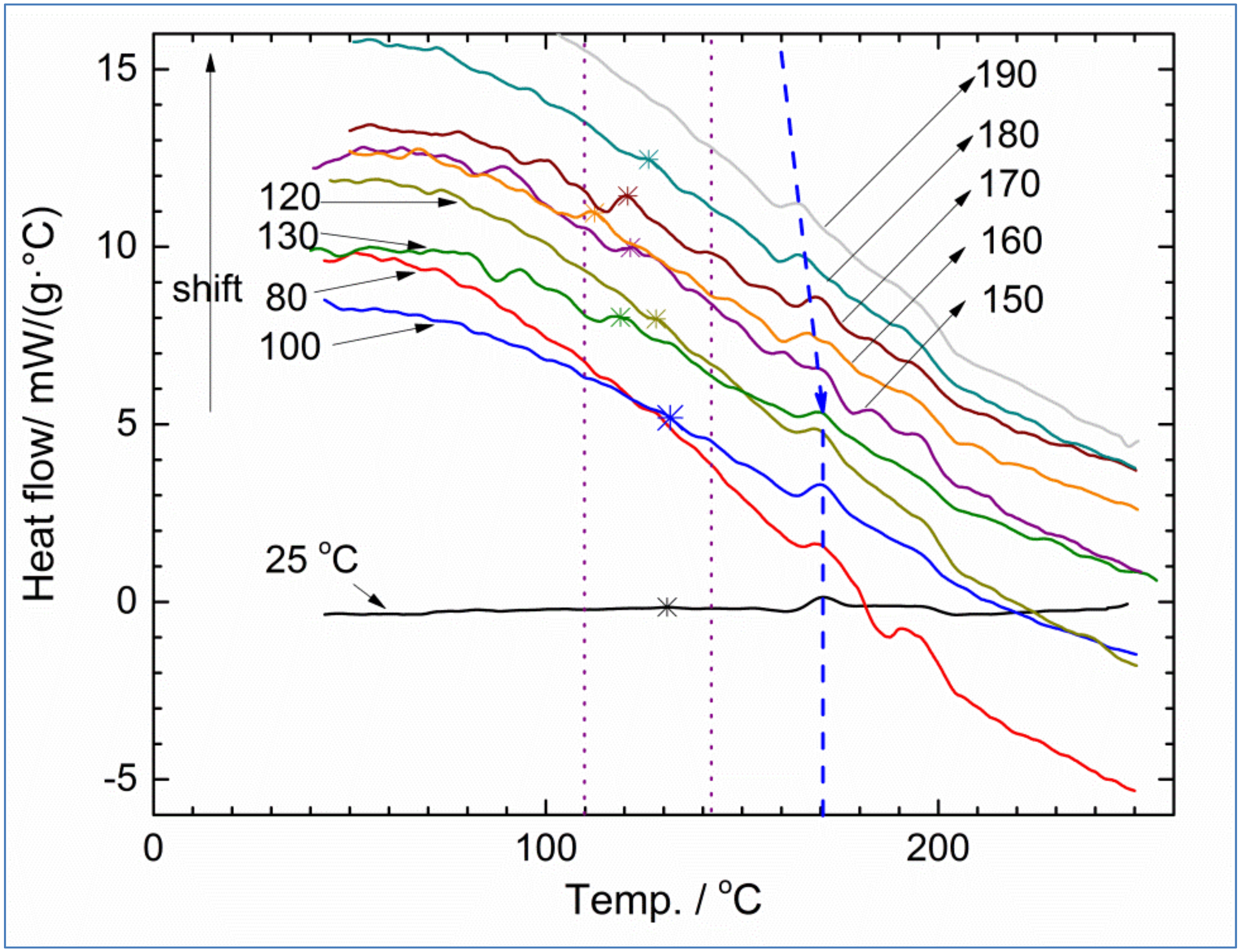


There appears to be a peak in the mechanical properties at around 130ºC.

Technical Accomplishments

LBNL

Characterization

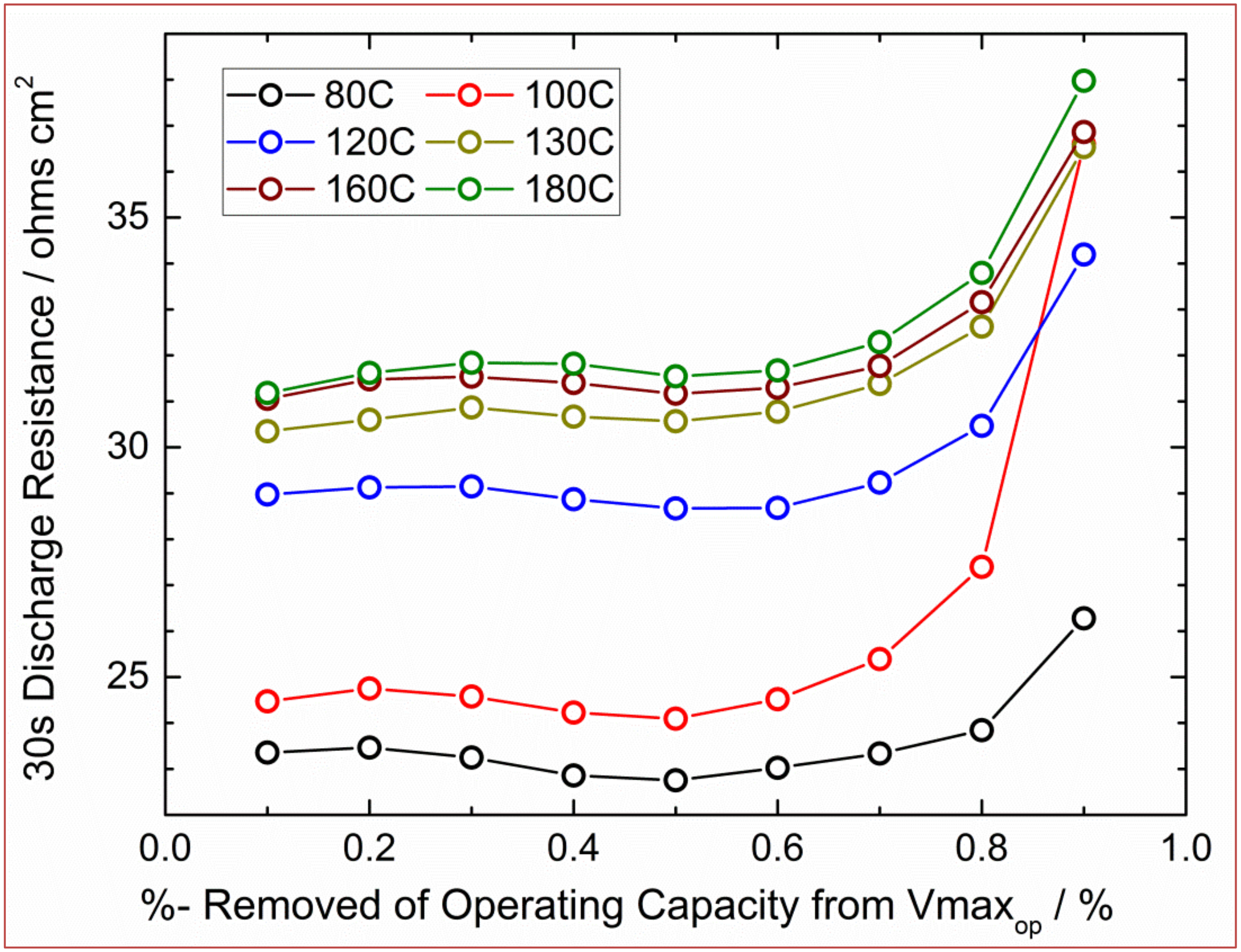


The melting temperature of the polymer in the laminate appears to decline as the drying temperature exceeds 130°C. May suggest smaller crystallites.

Technical Accomplishments

LBNL

Electrode power performance



The 30-sec pulse power resistance increases with drying temperature!

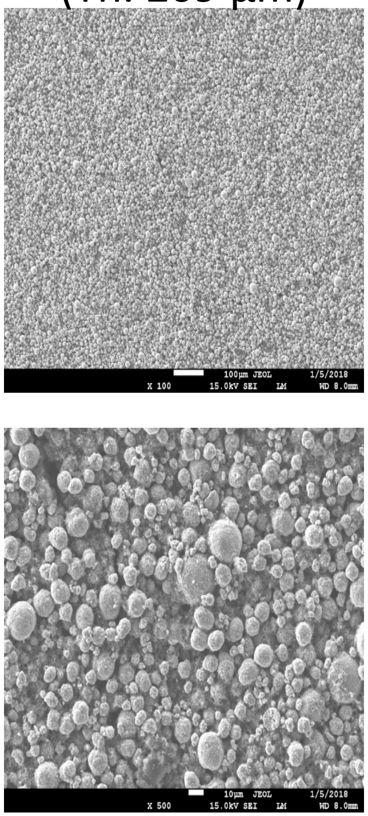
Technical Accomplishments

LBNL

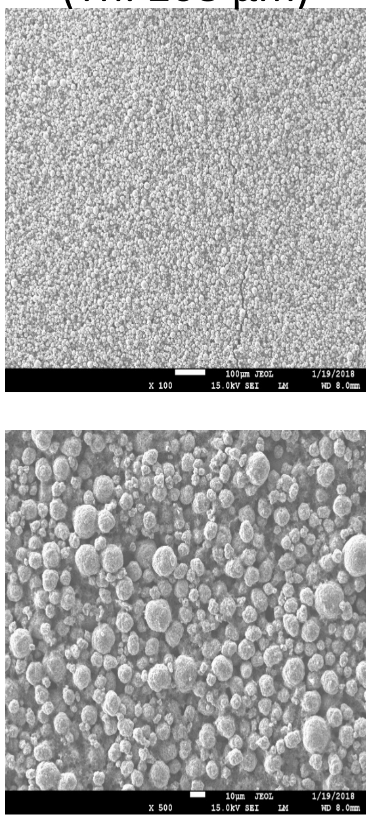
Preliminary Work

Bend test of binder mixtures (Kynar761/HSV900)

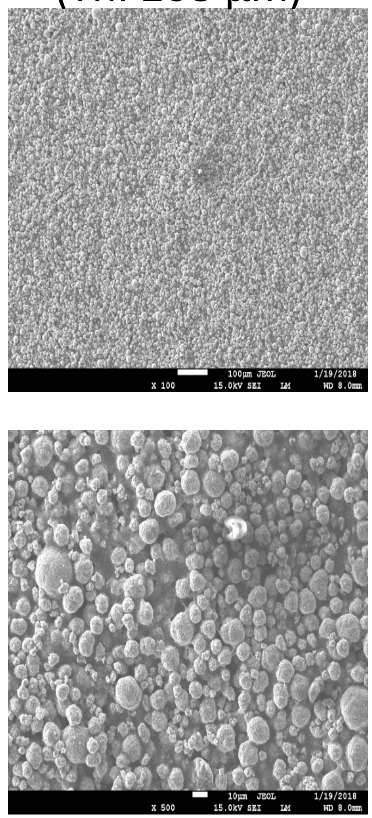
100/0- #8
roller
(Th. 209 µm)



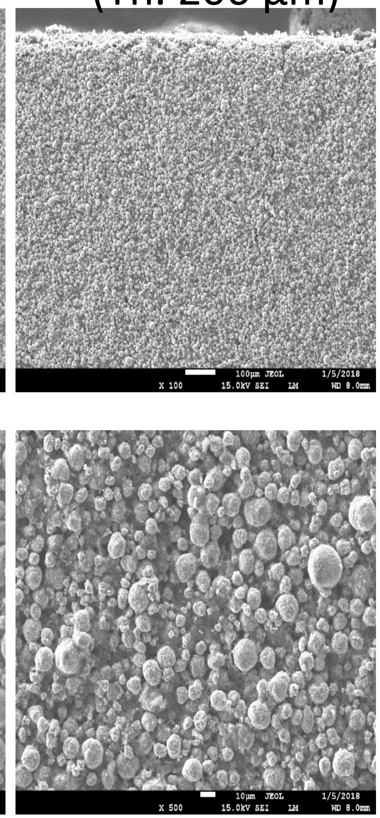
75/25- #8
roller
(Th. 208 µm)



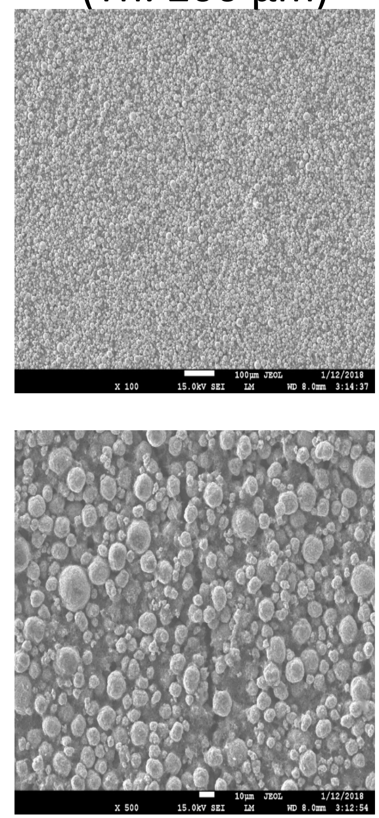
50/50- #9
roller
(Th. 208 µm)



25/75- #10
roller
(Th. 206 µm)



0/100- #8
roller
(Th. 206 µm)

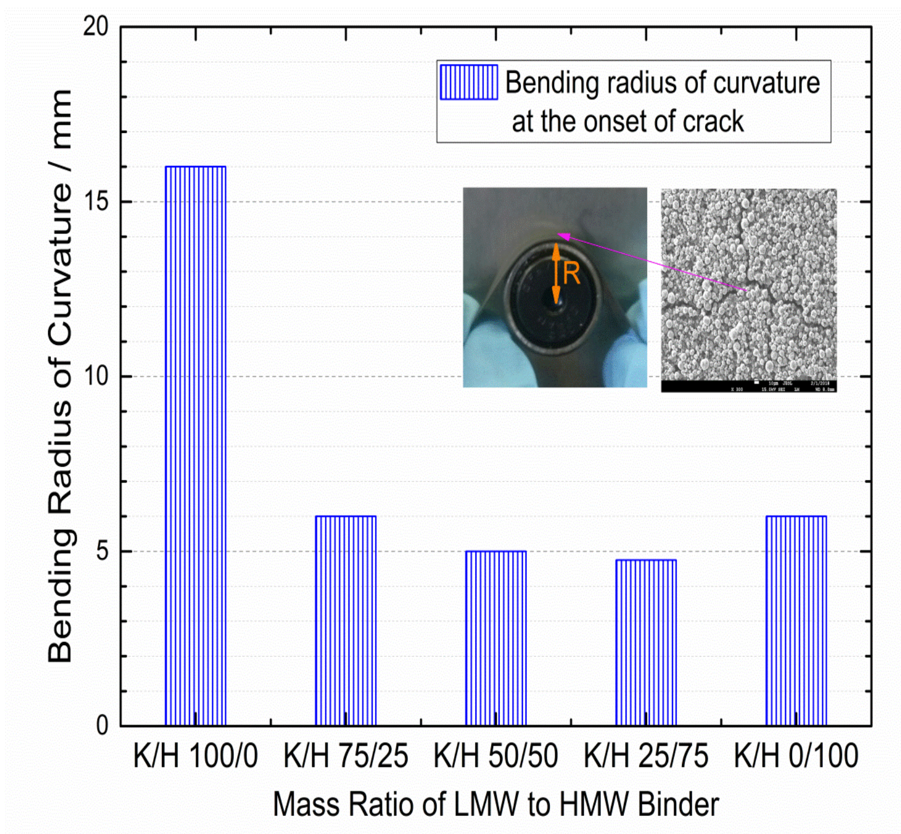


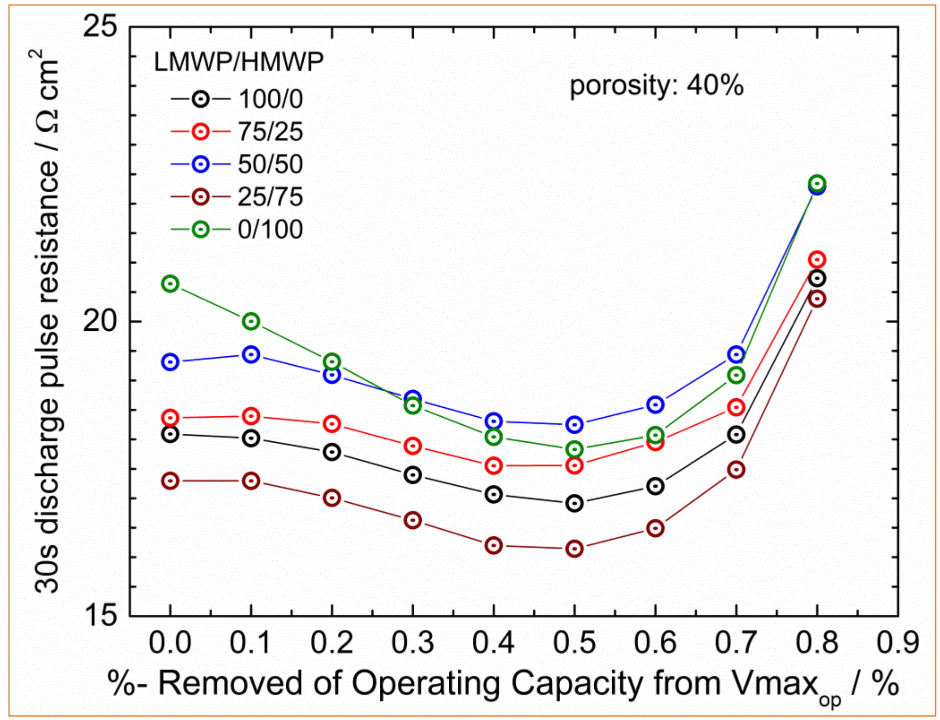
Technical Accomplishments

LBNL

Preliminary Work

Electrodes fabricated with a mixture Kynar761/HSV900





Preliminary results suggest there is an optimum in performance when a mixture of binders is used.

Remaining Challenges and Barriers

LBNL

What we know:

- The polymer is what holds the particles together and gives the electrode mechanical integrity.
- Electrodes of identical composition have much different mechanical and electrochemical properties depending on drying time/temperature.
- Surface tension and viscosity play important counter balancing roles during drying.
- Electrodes of higher molecular weight have better mechanical properties than electrodes of lower molecular weight.
- A blend of molecular weights may have the best properties of all.

Challenges:

- For an electrode that is only 3 % binder, by weight, where it is in the electrode or its configuration (level of crystallinity)?
- What has the greater effect, drying rate *or drying* temperature?
- How do the forces that led to the final configuration from slurry to dried electrode change with drying time?

Responses to Previous Year Reviewers' Comments

LBNL

- …address 1-3 significant questions/criticisms/ recommendations from the previous year's reviewers' comments…
  1. "The critical value that national laboratories can bring to industry is to investigate processes and materials of relevance to industry, but then to explain the phenomena in terms of fundamental understanding. That is lacking in this project."
     - Point taken. This is a 3 year project. Companies do not share their inabilities. We are methodically scoping the impact of every process on the fabrication of thick electrodes. In 2017, a lot of effort was spent on understanding the impact of calendering at different temperatures. In the end we determined that this was insignificant wrt thick electrode fabrication. This year we moved to drying at different temperatures.
  2. "… one wonders if this is repeating what industry already knows. "
     - It is true that up to now, we have focused on processes that are easily repeated and studied by industry. Our focus for the first two and a half years has been a scoping study of important processes. As we get into drying at industrial speeds, we are hitting on many critical competing physical processes that will require a more in-depth investigation where a national lab can make significant contributions.
  3. "…the PI ought to extend the area of evaluation beyond calendaring, e.g., mixing process, viscosity of slurry, drying temperature, particle size of powder *etc*."
     - In 2016 of the initial scoping study we evaluated mixing order and slurry viscosity, among other aspects of electrode fabrication. In 2017 we covered calendering at different temperatures. This year we are focused on drying speed. This appears to have the greatest impact on thick electrode performance and will therefore be the focus of our efforts in the time remaining (see Future Work).
  4. "It is not clear that the PI's choice of binders was focused on binders developed for thick flexible electrodes."
     - In the original SOW the only changes indicated of the binder would be the molecular weight. An investigation of binder chemistries would have been too broad for the resources available.

Collaboration and Coordination

LBNL

Partnerships / Collaborations	
ARKEMA	Provides binders of PVdF of different molecular weights, some blends, and some experimental binders.
umicore	Provided baseline active material.
BLACK DIAMOND STRUCTURES	Provides a conductive carbon additive that enhances the cohesive strength of the laminate.
DAIKIN	Provides battery-grade electrolyte.
BYU	Provides separators and performs calculations of the drying configurations of particles in electrodes.
Hydro Québec	Provides current collectors, other cell parts, equipment for making cells, and expertise on cell manufacturing.
APPLIED SPECTRA	Provides measurement of electrode composition as a function of depth from the surface.
BERKELEY LAB	Colleagues provide capabilities in macroscopic modeling and characterization of laminates using the techniques at the ALS and NCEM.

Proposed Future Work

LBNL

Any proposed future work is subject to change based on funding levels.

Six months remaining

Physical Properties of Slurry

- Measure the viscosity of the slurry as a function of temperature and solvent content
- Measure the surface tension of the slurry as a function of temperature and solvent content

Electrode Performance

- Use electrochemical techniques (*e.g.*, ac-impedance spectroscopy) to identify sources of impedance in electrodes dried at different temperatures

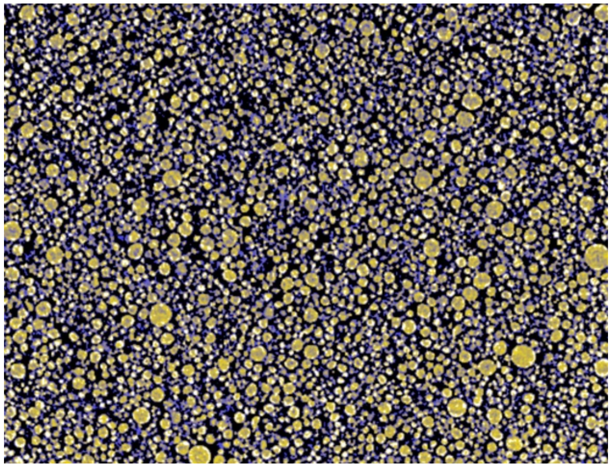
Further experiments with mixtures of binders

Polymer and Carbon Visualization

- Work with ALS on 3-D tomography of electrodes (dried and drying.)
  - Visualize and quantify differences in electrode morphologies from current collector to surface
- Try FIBS
- Try laser ablation with ICP

Preliminary results from ALS

- Lateral cross section of electrode
- Oxide is yellow; polymer is blue



Summary

LBNL

Relevance

- The work is focused on getting at the fundamental principles to producing high energy density electrodes, a top VTO priority. Advancements in this area should result in faster routes to producing high energy density cells.

Approach

- Scope out the effects of each process of cell manufacturing on the final properties of the electrode.
- Use bench scale techniques consistent with large scale manufacturing
- Measure critical properties as a function of temperature and solvent content
- Use standard and advanced diagnostics to provide understanding between materials, processing, and electrode quality.

Major Technical Accomplishments

- A methodology for producing thick electrodes that is on the order of industry production times.
- Determined that there is an optimum in mechanical performance as a function of drying temperature at *ca*. 130^{o}C.
- Determined that electrodes dried slowly (ca. 40 min. at 80^{o}C) perform better electrochemically than electrodes dried more quickly.

Future Work

- Measure the viscosity of the slurry at different temperatures
- Measure the surface tension of the slurry at different temperatures
- Identify the sources of the electrochemical impedance that are a function of drying time/temperature
- Perform more work at ALS to try to understand the polymer distribution in the electrode
- Use information to modify conditions such that electrodes perform well at moderately high drying rates.